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J. Perdomo, P. Singh, and P. Conde
S. Pawel

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# APPLICABILITY OF ELECTROCHEMICAL NOISE (ECN) MEASUREMENTS IN KRAFT PULPING LIQUORS

J.J. Perdomo*, P.M. Singh, P.R. Conde.

Corrosion and Materials Engineering Group, Institute of Paper Science and Technology, Atlanta, GA 30318-5794

S.J. Pawel

Corrosion Science and Technology Group, Oak Ridge National Laboratory

Oak Ridge, TN 37831-6156

ABSTRACT

The present study addresses the applicability of electrochemical noise (ECN) measurements for use as a corrosion probe in continuous kraft pulping digesters and other pulp mill equipment. Controlled ECN tests as well as weight loss measurements were conducted in pulping liquors for different materials using autoclaves. Conventional data treatment of the ECN parameters in both time and frequency domains did not correlate very well with the physical changes on the tested materials in kraft pulping liquors. Results from this study have shown that current biasing occurred on one of the electrodes in all tested conditions. For some of the environments tested, the currents measured did not correlate to the physical corrosion measurements. However, ECN currents did correlate to the redox reactions involved in the sulfur chemistry at the electrode surface. Larger variations in ECN currents with respect to their average in a given time record are believed to represent both sulfur redox reactions and iron dissolution for carbon steel

* Corresponding author: Institute of Paper Science and Technology, 500 Tenth St. NW, Atlanta, GA 30318-5794, email: jorge.perdomo@ipst.edu

electrodes, whereas relatively small fluctuations of the current are believed to represent purely the sulfur redox processes. Pulping liquor composition affects the magnitude of oxidation of sulfur species at the electrode surface as well as iron dissolution reaction. Cyclic voltammetry tests support the ECN observations that the sulfur redox reactions are taking place on the electrode surface in environments containing $Na_2S$ and that the relative extent of iron dissolution and sulfur oxidation reactions depend upon the amount of $Na_2S$. Small amounts of $Na_2S$ in the environment may inhibit iron dissolution, whereas larger amounts may increase it. This was corroborated by the corrosion rate measurements and the magnitude and variation of the current density from the ECN tests.

KEYWORDS: Steel, Kraft Liquor, Corrosion; Pulping, Black Liquor, Electrochemical Noise, Sulfur Chemistry, Cyclic Voltammetry.

## INTRODUCTION

Pulp and paper mills are susceptible to many forms of corrosion demand specialized material selection for different environments and equipment. In the case of the kraft pulping process, hot sulfide-containing caustic solution (white liquor) is used to remove the lignin that binds the cellulose fibers in wood chips. One such pulping process is carried out continuously in a large carbon or stainless steel vessel (digester) at temperatures that range between 130 and 170°C[1]. The resulting cellulose fiber, or pulp, is used to manufacture many products such as printing paper. Spent liquor is called black liquor and contains remaining NaOH and $Na_2S$, a large number of organic compounds from the wood chips, and chemicals formed during the pulping process. Although the

role of inorganic constituents has been related to the corrosion in laboratory tests[2-10], the role of wood extractives and other organic constituents in black liquors need to be better understood. Singh et al.[11] have provided evidence that if the pulping conditions and inorganics are kept the same, then the corrosivity of black liquors varies, and it is strongly dependent on the wood species being pulped, i.e., some black liquors are more corrosive than others. With such a wide range of corrosive environments in pulp mills and variations in the environment within the same piece of equipment like digesters, it becomes important to have a reliable on-line corrosion monitoring tool to have real-time assessment of the process. This will in turn help in relating process variables with the ongoing corrosion processes. One such on-line corrosion monitoring technique is electrochemical noise.

The basis of the measurement is that all corrosion processes cause spontaneous fluctuations of the free corrosion potential and the associated current. These fluctuations, termed electrochemical noise (ECN), and the analysis of the signal, may be used to interpret the underlying corrosion processes. Typically, the events take place at frequencies less than 1 Hz and show small currents (μA to mA) and small corresponding voltage change (μV to mV). The magnitude, duration, and frequency of the fluctuations can be used to determine the prevailing corrosion mechanism. The technique has been recently used in industrial applications, showing some promising results[12-14]. Improvements in digital signal and data acquisition and storage in the last forty years have made ECN measurements more attractive compared to when they were proposed[15-16]. Details of the technique have been extensively described elsewhere[17-22]. ECN measurements have been used in a number of systems to measure corrosion rates and to

differentiate among the mechanisms of corrosion[18]. Electrochemical noise (ECN) measurements have been proposed as an on-line probe to monitor the corrosion behavior of different materials in pulping liquors[12].

In systems like sulfide-containing caustic solutions, where redox reactions other than corrosion reactions are also possible at the electrode surface, the ECN signal can be very difficult to interpret and may not yield corrosion rates or mechanisms reliably. Some of the possible sulfur redox reactions reported at near carbon steel corrosion potentials in pulping liquors are[4,10,23]:

$$S_2O_3^{2-} + 6H^+ + 8e^- \Leftrightarrow 2S^{2-} + 3H_2O \quad (1)$$

$$S_2^{2-} + 2e^- \Leftrightarrow 2S^{2-} \quad (2)$$

$$8SH^- \Leftrightarrow S_8 + 8H^+ + 16e^- \quad (3)$$

Because of the complexity of the electrochemical processes involved in corrosion rate determination in kraft pulping liquors, the present study is aimed at exploring the feasibility of ECN technique to monitor corrosion in such systems.

## EXPERIMENTAL PROCEDURE

Initial work on this study was conducted to test the field equipment which is generally used for ECN measurements. Tests were designed to understand the effect of different constituents of pulping liquor on the ECN signal for different commonly used materials. ECN tests were carried out using a three-electrode configuration as shown in Figure 1. Samples were electrically isolated from the vessel. The current flowing between the two nominally identical electrodes due to electrochemical activities on their surface was monitored using a zero resistance ammeter. The corresponding potential noise was also

measured with respect to a third electrode ($Ag/Ag_2S$ reference electrode, SSSE) using a high-impedance voltmeter. The sampling rate in this work was set to 1 Hz. The experimental matrix is shown in Table 1. Solution composition, including inorganics for the black liquor from a pulp mill, is shown in Table 2.

Tests were carried out for different time periods, as shown in Table 1. Current and potential data collected during this time period were analyzed by measuring important ECN parameters from both time and frequency domains, namely, mean potential and current, standard deviation of potential and current, noise resistance, pitting index, impedance at low frequency, and roll-off slopes of power spectra density plots as discussed earlier[22]. Additionally, current integration was used to get the total charge transfer which was further used in Faraday's law to yield a theoretical corrosion rate[12]. After each test the electrodes were removed and examined for localized corrosion and film characteristics. The film was removed and the samples were weighed to get general corrosion rates. This value was compared with the corrosion rate calculated from the ECN current integration. Film was removed using an ASTM G1 standard procedure which uses inhibited acid cleaning solutions[24]. The ECN tests were conducted under stagnant conditions at 135°C (302°F) using a 2205 (UNS S31803) autoclave with 3-liter capacity. Three materials were tested in this study, namely, carbon steel A516 grade 70 (UNS K02700), stainless steel 304L (UNS S30403), and platinum (UNS P04995).

Steel electrodes were polished to 600-grit paper, whereas Pt electrodes were acid cleaned in 0.1 N HCl solutions. All electrodes were cleaned with acetone and rinsed with deionized water prior to the tests. The surface area of each working electrode was approximately 10 $cm^2$. The reference electrode used for both synthetic and black liquors

tests was a silver-silver sulfide couple, $Ag/Ag_2S$ (SSSE). However, the results here were converted and have been reported versus standard hydrogen electrode (SHE)[25].

In order to characterize the electrochemical reactions on the carbon steel (A516 grade 70 (UNS K02700)) surface, cyclic voltammetric tests were also performed in a glass cell in the same solutions shown in Table 2 at room temperature using a standard calomel electrode (SCE). The results were also converted and have been reported versus standard hydrogen electrode (SHE)[25]. The steel electrodes were cylindrical in shape with a total surface area of approximately 10 $cm^2$. Prior to use, steel specimens were polished with a series of SiC papers up to 600 grit, degreased with acetone, and rinsed with double-distilled water. Finally, the electrodes were electrochemically cleaned in the cell by cathodically polarizing them for one minute.

Solutions were deaerated with argon gas for 30 minutes prior to and during cyclic voltammetry tests. A cyclic voltammetry (CV) test was also carried out in deaerated 18.5 g/L NaOH as a reference to see the effect of $Na_2S$ additions on the electrochemical activity. A total of 10 potential scan cycles were carried per solution (see Table 2) at the scan rate of 50 mV/s. All CV tests started at the open circuit potential (OCP) and the potential was first changed in the anodic (forward) direction.

## RESULTS AND DISCUSSION

Figure 2(a) shows both the current and voltage time data for carbon steel A516 grade 70 (UNS K02700) exposed to Synthetic I+ liquor at 135°C over four days. Theoretically, if the rate of reaction is the same on the two working electrodes, then the average of current noise from both electrodes should be zero. However, in the present set of experiments the average current signal was a nonzero value. This is also called biasing and it

indicates that one of the two electrodes is more active for a variety of possible reasons which generally cannot be easily controlled in an experiment.

For the test shown in Figure 2(a) no current spikes were observed during the four-day exposure other than what happened in the first few hours during heating of the vessel. Current spikes are generally attributed to pitting activity on the surface of the electrode[17]. Open circuit potential, on the other hand, increases in the first few hours of the experiment and then decreases slowly over the entire test period as shown in Figure 2(a). Results shown in Figure 2(b) show the calculated pitting index as a function of testing time. The pitting index values were calculated by dividing the standard deviation of current by the root mean square of the current in the same time interval[19,26]. For most of the test duration, the pitting index values for this test were below 0.1 for these calculations, whereas a pitting activity generally is represented by the pitting index values approaching 1.0[19,26]. Clearly, one such event was recorded in this test after about 4.2 hours of exposure. However, physical examination did not show any signs of pitting on either of the electrodes.

Another way to analyze such data is by using the roll-off slope approach of both current and voltage power spectra densities, as shown in Figure 2(c). In this type of analysis, first the data from the time record measurement are converted into a frequency equivalent by means of either a fast Fourier transformation (FFT) or maximum entropy method (MEM)[17,18]. The essence of the former is to represent the time record as a waveform that can be decomposed into a sum of sinusoids of different frequencies and specific amplitudes and phases. MEM computes the coefficients of a particular class digital filter that would give the observed time record when applied to white noise input

signal. MEM mathematically ensures that the fewest possible assumptions are made about unmeasured data by choosing the spectrum that is the most random or has the maximum entropy for the process under investigation. So, every time domain function has a counterpart in the frequency domain. The counterpart function is called Power Spectra Density (PSD) and indicates how the sequences of power or energy are distributed in the frequency domain[17,18].

In this case the slopes are more positive than -20 db/decade criterions, which tends to indicate pitting[27-30]. Although no pitting was observed, some areas showed preferential corrosion attack on the surface of both electrodes (Figure 2(d)). The extent of the areas with preferential corrosion attack varied for the two working electrodes. This may be associated with the current biasing observed in Figure 2(a) for this test. The reason for preferential corrosion attack may be due to local microstructure variation in the metal but could not be confirmed at this moment. However, it is believed that other minor differences between the two "nominally identical" electrodes (e.g., surface finish, size, temperature variations, and solution composition) may also be responsible for current biasing in ECN measurements. Cottis[18] explains that small pH changes may occur as a result of the net current between the two electrodes, where the nonpitting electrode will act as a cathode, and the neighboring solution becomes more alkaline as a consequence of this behavior; this is thought to inhibit pitting. The pitting electrode is said to be a net anode causing the pH to drop, facilitating pitting. It is unclear whether the explanation offered by Cottis[18] will describe the current bias observations and preferential corrosion attack in the highly alkaline solutions tested in this study.

Current and potential data from the ECN tests were used to obtain the noise resistance ($R_n$) as described elsewhere[17,18,21,22]. Noise resistance is obtained by dividing the standard deviation of potential in a given time segment by the standard deviation of the current corresponding to the same time interval. This parameter is equivalent to the polarization resistance, $R_p$, and can be used to yield corrosion rates. However, the Stern-Geary constant is needed to calculate the corrosion rate from $R_n$ data. The noise resistance parameter can either be calculated from average current and potential values over the entire test period or for the small segments of time separately to check corrosion activities at a particular time. In the case of carbon steel A516 grade 70 (UNS K02700) in Synthetic I+ solution, $R_n$ calculations were carried out in both time and frequency domains. Figure 2(e) shows $R_n$ values calculated where each point represents the value of noise resistance calculated from current and potential data over one-hour intervals. The average noise resistance over the entire test shown in Figure 2(e) was ~0.2 kohm. A different result is obtained when power spectra density plots for impedance are used (Figure 2(f)). The low-frequency limit of the impedance for both fast Fourier transformation, FFT, and maximum entropy method, MEM, represent the noise resistance[17]. These calculations are in the order of ~3 $10^{-3}$ μohm at the lowest frequency measured.

Because of the discrepancy observed between both noise resistance calculations, i.e., in the time and frequency domains, corrosion rate estimation cannot be made correctly. Even by assuming that the time domain $R_n$ yields a more meaningful result than its frequency equivalent, and assuming typical Tafel constant approximations of approximately 100 mV for both anodic and cathodic slopes, which will give a Stern-

Geary constant of 22 mV[27], the calculation will yield a corrosion rate of 0.25 mm/y (9.5 mpy) for the data shown in Figure 2(a). This value is much smaller when compared to the actual weight loss measurement giving a corrosion rate 7.3 mm/y (277 mpy). This result indicates that all current involved in the corrosion of the electrodes is not registered in the ECN data. This is especially true for large electrodes where the local anode/cathode areas may form on the same electrode, and only a small current may flow from one electrode to another, which is registered by ECN. In order to obtain such a large corrosion rate a Stern-Geary constant of 652 mV is required (Table 3). The physical basis of such a large Stern-Geary constant would be difficult to justify based on the mechanism for overvoltage in electrochemical tests. In a previous ECN study stainless steel electrodes were tested in NaCl solution[22]. Results from that study gave relatively accurate corrosion rate and mechanism prediction as the corrosion was the only electrochemical reaction occurring on the electrode surfaces[22]. In the present study many of the calculations ($R_n$, pitting index, etc.,) may not simply apply on this situation due to the presence of $Na_2S$ in caustic solutions, where sulfur redox reactions are possible on the electrode surface. Therefore, only the interpretation of current/potential transients and their quantitative comparisons could yield meaningful information.

ECN data from other tests, listed in Table 1, were also analyzed using a similar approach to the one described above. Table 3 summarizes the relevant ECN parameters calculated. In all the tests performed in the present study average current values were not zero and were generally biased.

Data in Table 3 indicate that for the tests where electrodes showed significant weight change the corrosion rate calculations by weight loss, noise resistance, and current

integration do not match. Only cases where weight loss yielded zero corrosion rates may be assumed as suitable for fitting small Stearn - Geary constants ($B$) on the order of 20 millivolts to yield a zero corrosion rate. Cases where weight loss measurements exhibited large corrosion rates require $B$>>20mV. The sulfur redox reactions at the surface of the electrodes will affect the magnitude and variations of the currents measured, which in turn will affect the calculations of the noise resistance parameter, $R_n$.

Corrosion rates calculated by integration of current flow during the test and by using Faraday's law gave values which were in general lower than what was measured from weight loss. This can be physically explained as follows. The current measured between the two "nominally identical" electrodes through the zero resistance ammeter (ZRA) is only the current that flows between the two electrodes. However, on a large electrode, adjacent areas may act as cathode next to an active anode. This means that the only recorded current signal will be in cases where one electrode acts as an anode and the other as a corresponding cathode and vice versa. Therefore, only a fraction of the total corrosion current will pass through the ammeter and will be recorded. That is to say that there is an important size effect of the electrode in terms of the current that can be measured. Larger electrodes are expected to have many random anodic and cathodic sites on each surface.

In tests with platinum or stainless steel electrodes, even though there was no physical corrosion measured, there was a significant current, especially in solutions containing $Na_2S$ as shown in Table 3. In these cases the current can be attributed to redox reactions on the electrode surface. This points to the possibility of error introduction in corrosion rate measurements in such systems if ECN traditional signal analysis is used alone.

Neither time nor frequency domain analysis of ECN data seem to consistently predict the pitting susceptibility of the electrode material in the sulfide-containing environments (Table 3). Pitting occurred in few instances, as noted in Table 3, but the traditional ECN data analysis failed to predict consistently the type of corrosion. This can be explained by the fact that sulfur (redox) reactions on the metal surfaces may account for some of the current activity. Data manipulation to calculate the corrosion rate requires only the amount of current due to the corrosion process. However, it is difficult to separate current signals due to corrosion reactions and other redox reactions on the electrode surface.

Figure 3(a) depicts the value of average current, shown in Table 3, for carbon steel in various environments tested in an autoclave under stagnant conditions at 135°C. The absolute value from Table 3 was taken since the actual sign of the current represents that one electrode was more active with respect to the other. In the same experiments in the tested matrix, the standard deviation for ECN current, and its root mean square (RMS) value, were much larger than the absolute value of the average current. This represents a large spread of the current values measured in a given test. Figure 3(b) depicts the potential measurements (vs. SHE) for the same tested conditions. It can be seen that increased sulfidity (addition of $Na_2S$) makes the open circuit potential slightly more positive. Corrosion rates for the tested materials calculated from weight loss are shown in Figure 3(c). Note that despite the fact that current events were registered (see Figure 3(a)), not all tested conditions provided measurable weight loss (Figure 3(c)). Measurable corrosion for carbon steel electrodes was only detected in $H_2O$, Black Liquor I+, Synthetic I+, and 25% White Liquor with 75% Black Liquor I, whereas other test

environments did not show detectable corrosion rates on carbon steels. No pits were observed upon inspection, other than the localized attack in the Synthetic I+ solution described earlier. By comparing Figure 3(a) and 3(c), it can be seen that only current measurements that had larger variation of currents with respect to their average showed general corrosion rates. The larger the variation (standard deviation) with respect to its average, the larger the corrosion rate. This is an interesting result produced by biasing where the magnitude of the bias is related to the corrosion rate. For both Black Liquor I and Synthetic Liquor I with low sulfidity the average currents were similar to its standard deviation. However, the current in sulfide-containing solutions does not represent the dissolution of iron alone but may also involve current produced by other redox reactions at the electrode surface. Two types of electrochemical activities may produce the total current measured: a portion of the current is due to redox reactions other than corrosion reactions, whereas the second fraction is due to the dissolution of iron in cases where variation is much larger than the average current record. If redox reactions other than the corrosion reactions are happening to the same extent at the surface of both working electrodes, then their effect should be similar on the ECN current signal from both electrodes. However, this does not seem to be the case; the rates at which these redox processes are happening are not the same on both electrodes, causing one electrode to be more active than the other. If electrodes get biased, then one of the electrodes with open circuit potential closer to the redox potential for sulfur reaction may favor this reaction on its surface. The differentiation of the open circuit potential of each individual electrode cannot be made since the value measured through this technique represents the average

potential of the pair of working electrodes as if they were one, as shown schematically in Figure 1.

Stainless steel electrodes tested under the same conditions as carbon steel did not reveal similar ECN behavior. Weight loss for stainless steel was negligible with the exception of two environments, i.e., Black Liquor I+ and 25% White Liquor with 75% Black Liquor I. Even in these two environments, the corrosion rates reported were below 0.025 mm/y (1 mpy) (see Table 3). General corrosion rates obtained by weight loss for carbon and stainless steels in the environments of this study are in agreement with previous published results[11]. Additionally, no pitting was observed upon inspection of the stainless steel electrode surfaces after testing. Large variations in current with respect to average current values were observed but no correlation to the actual corrosion rates could be made. Absolute average currents for the stainless steel tests were smaller than those for carbon steel under otherwise similar conditions except for the test in Synthetic I environment where the currents on stainless steel were higher than that for the carbon steel in an equivalent test. However, the currents measured in the tests with stainless steel are believed to be mainly due to sulfur chemistry redox reactions on the electrode surface.

Even though there was no weight change, but there was current signal in the ECN tests carried out, platinum electrode data in Table 3 show that the absolute average current values were small with a relatively large standard deviation. This behavior is similar to what is observed on stainless steel electrodes where significant current was detected indicating redox reactions, but no measurable weight loss was observed on either electrode.

Cyclic voltammetry tests in the present study were performed on carbon steel at room temperature under stagnant conditions to study the effect of temperature and composition on the electrochemical activity on carbon steel electrodes. Previous work on a similar system has shown that temperature seems to raise the current by thermal activation whereas stirring, simulating flow, seems to decrease it, probably by removal of electrochemically active species from the electrode surface at the tested potentials[23].

Figure 4(a) shows ten cyclic voltammograms carried out in sodium hydroxide where oxidation of iron has been known to occur with the increase in potential[23]. Shoesmith et al.[23] attributed peaks at the position $I_a$ and $II_a$ for the forward scan in Figure 4(a) to oxidation of iron $Fe_3O_4$ and $Fe_2O_3$, respectively, whereas peaks $II_b$ and $I_b$ for the return scan correspond to the reduction of species formed at potentials corresponding to peaks $II_a$ and $I_a$, respectively. Note that the oxidation and reduction peaks become more prominent with every cycle. This means that the reactions are happening at higher rates as the number of polarization scans increases. This means that there is no scale buildup during each cycle and that the surface is renewed by the removal of the oxidation and reduction of species away from the surface with each cycle.

Figure 4(b) shows the 10th cycle for three different tests with different environments, namely, 18.5 g/L NaOH, Synthetic I, and Synthetic I+. Voltammograms in Figure 4(b) show that an addition of $Na_2S$ inhibits the oxidation peaks $I_a$ and $II_a$ to some extent, as shown by the data for Synthetic I liquor compared to the pure NaOH solution test. This suggests that the corrosion reactions for iron may be suppressed by $Na_2S$ additions under the tested conditions, and therefore Synthetic I and Black Liquor I environments experience no weight loss.

Cyclic voltammograms of carbon steel in sulfide-containing liquors show two additional peaks, as shown in Figure 4(b) at around –0.2 V and –1.15 V vs. SHE, labeled $III_a$ (oxidation) and $III_b$ (reduction), respectively, which have been attributed to the electrochemical reaction of $S_8$ as shown in Equation (3)[23]. The presence of peaks $III_a$ and $III_b$ support that sulfur chemistry reactions, e.g. Equation (3), may take place on the surface of the steel sample. However, the average open circuit potential (OCP) for Synthetic I and Synthetic I+ liquors at 135°C locates around -700 and -600 mV vs. SHE, respectively. Though the voltammograms were conducted at room temperature, increments in temperature will increase the magnitude of the peaks at which the reactions occur, shifting the entire voltammograms to the left[23]. Therefore, it is likely that the aforementioned OCP's of carbon steel in Synthetic I and I+ environments fall in the vicinity of reaction (3).

A similar result is also obtained for the black liquor with and without increased sulfidity as shown in the 10th cycle of Figure 4(c). However, the magnitude of the currents was lower for the black liquors compared to the test in equivalent synthetic liquors. Increased sulfidity (see Figures 4(b) and 4(c)) makes peaks $I_a$ and $II_a$ more noticeable. This means that iron oxidation is taking place at a higher rate than that observed in Synthetic I and Black Liquor I environments. This also confirms the weight loss results reported in Table 3. Open circuit potential measured during ECN tests at high temperature for Liquor I and Liquor I+ environments was close to -680 and -560 mV vs. SHE, respectively. Using the same argument described for synthetic liquors, it is possible that the OCP's for carbon steel in black liquors will also fall in to the vicinity of the reaction (3) shown in peak $III_a$.

Another important feature is that increasing the amount of $Na_2S$ increases the current at higher potentials, lifting the right portion of the voltammograms into the anodic region even during the reverse (cathodic) scan, i.e., current densities become more anodic. This may be explained due to the sulfur species being adsorbed on the electrode surface, which may undergo oxidation at a smaller rate even when potentials are scanned in the reverse direction. This would typically occur at the open cell potentials recorded for both synthetic and actual liquors shown in Table 3 at around ~ -600 mV vs. SHE. So there might be a competitive effect between iron dissolution and sulfur chemistry depending on the amount of sulfur available as described above.

Current densities for the carbon steel in cyclic voltammetry tests with Synthetic I+ solutions were higher when compared to the similar test in Black Liquor I+. Corrosion rates for ECN test electrodes in the same environment also show higher corrosion rates for Synthetic I+ solutions when compared to the similar test in Black Liquor I+ as shown in Table 3. Although there was the same composition of inorganics in the liquors as shown in Table 2, the less corrosive nature of this black liquor may also be due to the inhibiting action of some of the organic wood extractives as it has been pointed out by previous work carried out by Singh et al.[11].

## CONCLUSIONS

In electrochemical systems where redox reactions other than corrosion reactions may take place on the surface of electrodes, it is difficult to obtain the information on corrosion rate and mechanism from traditional ECN data analysis.

Platinum electrodes and stainless steel electrodes did not show any measurable corrosion rates in the pulping liquors tested. However, the ECN current signal for these tests was significant, showing that redox reactions including sulfur species were active on the electrode surfaces.

In all tested systems in this study, generally one of the two working electrodes shows more anodic activity than the other as indicated by current biasing.

Electrodes which showed significant corrosion through weight change measurements also exhibited larger variation of ECN current with respect to their average current values. This indicates that the presence of the corrosion reaction along with the sulfur redox reaction at the electrode surface may lead to a large variation in electrochemical activity. However, ECN tests on carbon steel electrodes that had a relatively small variation of current compared to the average current value showed insignificant corrosion rates. In these cases, a significant portion of the current measurements are believed to represent sulfur redox activity through the ECN.

Cyclic voltammetry tests clearly showed that sulfur redox reactions may take place on the electrode surface in $Na_2S$ environments. Results also indicate that there is a competitive effect of the presence of $Na_2S$ on iron dissolution, and the extent of sulfur redox reactions seems to depend on the amount of $Na_2S$ in the tested solution. Small amounts of $Na_2S$ may inhibit iron dissolution, whereas larger amounts may increase it. This was corroborated by the weight loss corrosion rate calculations obtained and the magnitude and variation of the current density signals obtained in ECN tests.

Synthetic liquors with increased sulfidity proved to be more corrosive than the black liquor with increased sulfidity. This has been attributed to the inhibiting action of some

wood extractives present in black liquors, which may affect the corrosion behavior of steel.

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TABLE 1. TEST MATRIX FOR ECN STUDIES.

| Material | Solution | T/[°C] | Time/[d] |
|---|---|---|---|
| CSA516 | Synthetic I | 135 | 11 |
| SS304L | Synthetic I | 135 | 7 |
| Pt | Synthetic I | 135 | 7 |
| CSA516 | *Synthetic I+ | 135 | 4 |
| SS304L | *Synthetic I+ | 135 | 4 |
| Pt | DI $H_2O$ | 135 | 2 |
| CSA516 | DI $H_2O$ | 135 | 5 |
| SS304L | DI $H_2O$ | 135 | 5 |
| CSA516 | Black Liquor I | 135 | 5 |
| SS304L | Black Liquor I | 135 | 5 |
| CSA516 | *Black Liquor I+ | 135 | 5 |
| SS304L | *Black Liquor I+ | 135 | 5 |
| CSA516 | 25%WL/75% BL I | 135 | 4 |
| SS304L | 25%WL/75% BL I | 135 | 4 |

*Ten-time increase sulfidity with respect to I

TABLE 2. SOLUTION COMPOSITION AND CONCENTRATIONS IN [g/L].

| **Solution** | **$Na_2S$** | **NaOH** | **$Na_2S_2O_3$** |
|---|---|---|---|
| Synthetic I | 6.79 | 18.75 | 4.09 |
| Synthetic I+ | 84.85 | 18.75 | 4.09 |
| Black Liquor I | 1.58 | 7.61 | - |
| Black Liquor I+ | 79.64 | 7.61 | - |
| White Liquor | 50 | 150 | - |

Synthetic solutions prepared with ACS-grade chemicals

TABLE 3. SUMMARY OF RESULTS OF ECN TESTS CONDUCTED IN DIFFERENT ENVIRONMENTS RELEVANT TO PULPING LIQUORS.

| Material | Solution | AVE I [A/cm$^2$] | STD I [A/cm$^2$] | RMS I [A/cm$^2$] | AVE E [V-SHE] | STD E [V-SHE] | AVE Rn [kOhm] | *$CR^{NR}$ [mm/y] | $CR^{CI}$ [mm/y] | $CR^{WL}$ [mm/y] | PI | ROS [dB/dec] | Pit. Obsrv. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CS | DI $H_2O$ | -4.32E-07 | 1.25E-06 | 1.32E-06 | -0.219 | 0.152 | 3.0 | 0.010 | 0.011 | 1.064 | Yes | >-20 | No |
| CS | Liquor I | 5.78E-07 | 6.27E-07 | 8.52E-07 | -0.682 | 0.030 | 1.4 | 0.000 | 0.009 | 0.000 | Yes | >-20 | No |
| CS | Liquor I+ | 4.36E-07 | 8.68E-07 | 9.71E-07 | -0.561 | 0.013 | 0.1 | 0.292 | 0.009 | 3.494 | Yes | >-20 | No |
| CS | Synthetic I | 1.13E-10 | 7.17E-12 | 1.13E-10 | -0.709 | 0.020 | 13645.2 | 0.000 | 0.000 | 0.000 | No | >-20 | No |
| CS | Synthetic I+ | -1.07E-06 | 3.22E-06 | 3.40E-06 | -0.620 | 0.067 | 0.2 | 0.247 | 0.075 | 7.303 | Yes | >-20 | Locals |
| CS | 25%WL+75%BL | -2.37E-07 | 1.04E-06 | 1.07E-06 | -0.569 | 0.021 | 0.2 | 0.094 | 0.006 | 0.085 | Yes | >-20 | No |
| SS | DI $H_2O$ | -2.02E-07 | 1.95E-07 | 2.81E-07 | -0.840 | 0.093 | 115.3 | 0.000 | 0.002 | 0.000 | Yes | >-20 | Yes |
| SS | Liquor I | -1.98E-07 | 2.95E-07 | 3.55E-07 | -0.692 | 0.015 | 15.1 | 0.000 | 0.003 | 0.000 | Yes | >-20 | No |
| SS | Liquor I+ | -2.40E-07 | 4.56E-07 | 5.15E-07 | -0.726 | 0.010 | 5.5 | 0.004 | 0.004 | 0.010 | Yes | >-20 | No |
| SS | Synthetic I | -8.11E-07 | 1.88E-06 | 2.05E-06 | -0.742 | 0.044 | 3.7 | 0.000 | 0.012 | 0.000 | No | >-20 | No |
| SS | Synthetic I+ | 4.20E-07 | 1.41E-06 | 1.47E-06 | -0.760 | 0.015 | 11.3 | 0.000 | 0.003 | 0.000 | Yes | >-20 | No |
| SS | 25%WL+75%BL | -2.40E-07 | 8.18E-07 | 8.53E-07 | -0.712 | 0.014 | 3.9 | 0.009 | 0.005 | 0.005 | Yes | >-20 | No |
| Pt | DI $H_2O$ | -4.58E-09 | 1.91E-08 | 1.97E-08 | -0.671 | 0.001 | 59.4 | 0.000 | 0.000 | 0.000 | Yes | >-20 | No |
| Pt | Synthetic I | 1.75E-09 | 8.00E-08 | 8.01E-08 | -0.671 | 0.001 | 11.3 | 0.000 | 0.000 | 0.000 | Yes | >-20 | No |

CS: Carbon Steel; SS: Stainless Steel
GC: Glass Cell; AC: Autoclave; PD: Pilot Digester
MAR: Moving Average Removal
CS: Carbon Steel, SS: Stainless Steel
PI: Pitting Index; B: Stern-Geary Constant; ROS: Roll-off Slopes
NR: Noise Resistance; CI: Current Integration; WL: Weight Loss
*corrosion rate calculations assume a Stern-Geary constant of 22 mV.

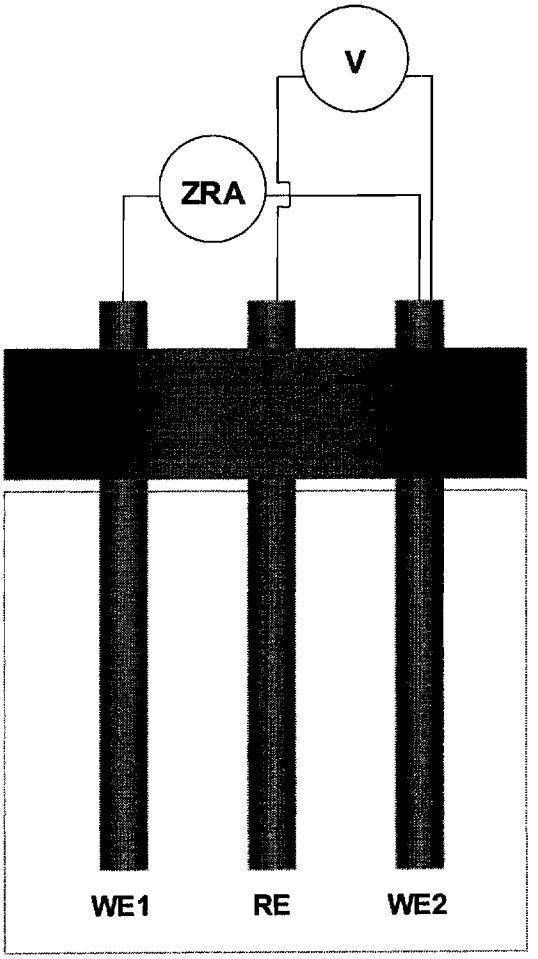


FIGURE 1. ECN cell configuration.

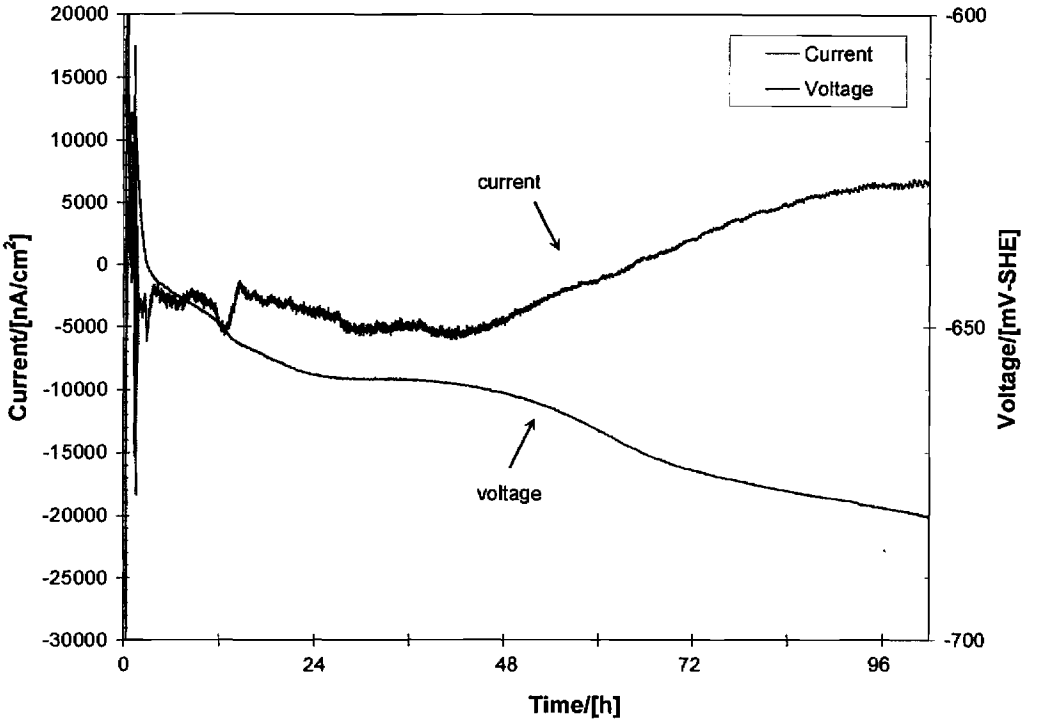


FIGURE 2(a). Voltage and current records in the time domain for carbon steel A516 grade 70 (UNS K02700) in Synthetic I+ solution over four days at 135°C.

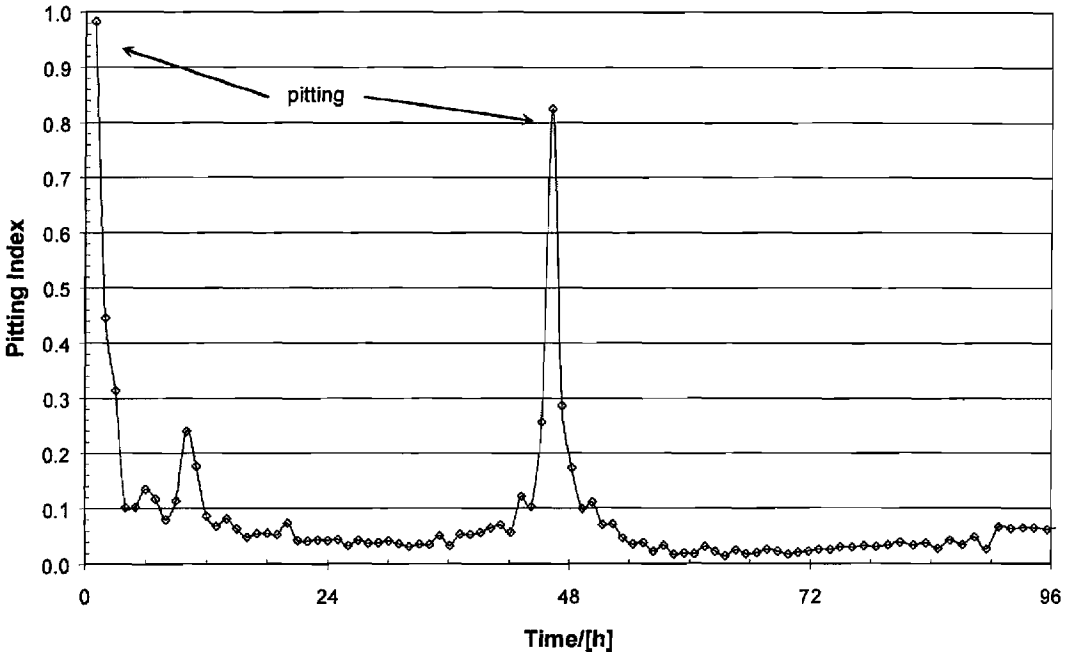


FIGURE 2(b). Pitting index as a function of time for carbon steel A516 grade 70 (UNS K02700) in Synthetic I+ solution over four days at 135°C.

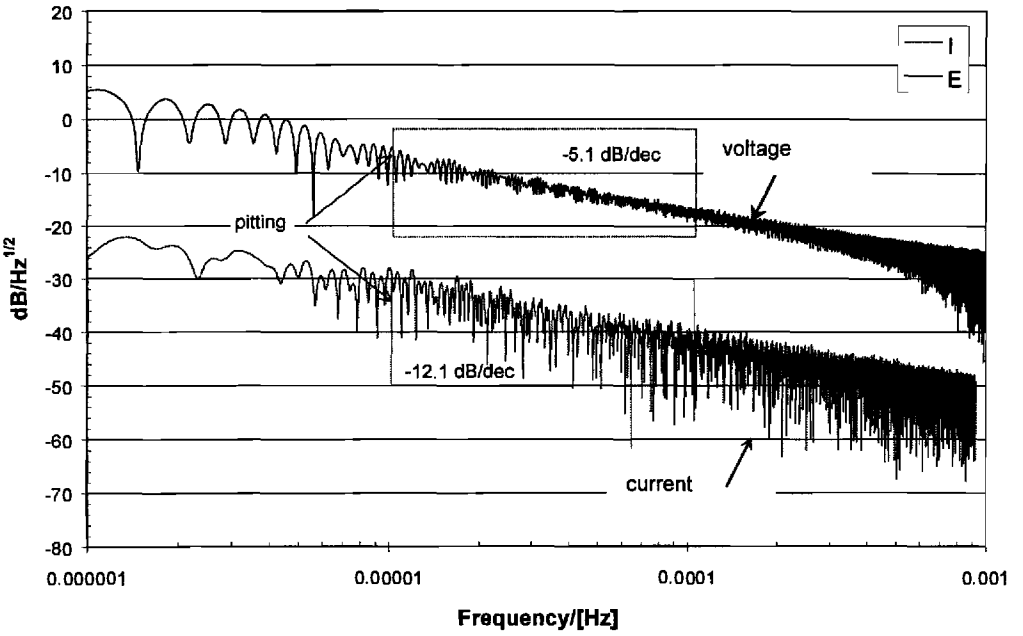


FIGURE 2(c). Power spectra density in the frequency domain for carbon steel A516 grade 70 (UNS K02700) in Synthetic I+ solution at 135°C.

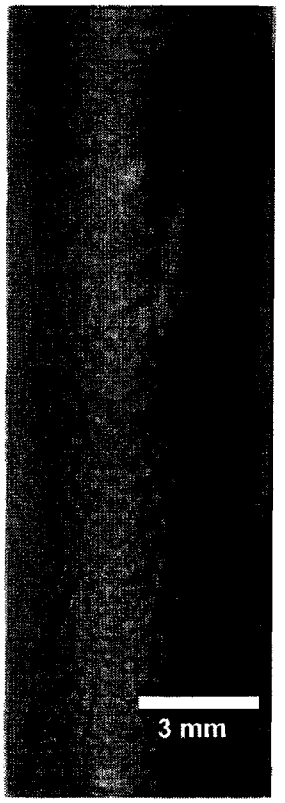


FIGURE 2(d). Physical appearance of carbon steel A516 grade 70 (UNS K02700) in Synthetic I+ solution at 135°C after testing for four days. Note orange-peel-like surface.

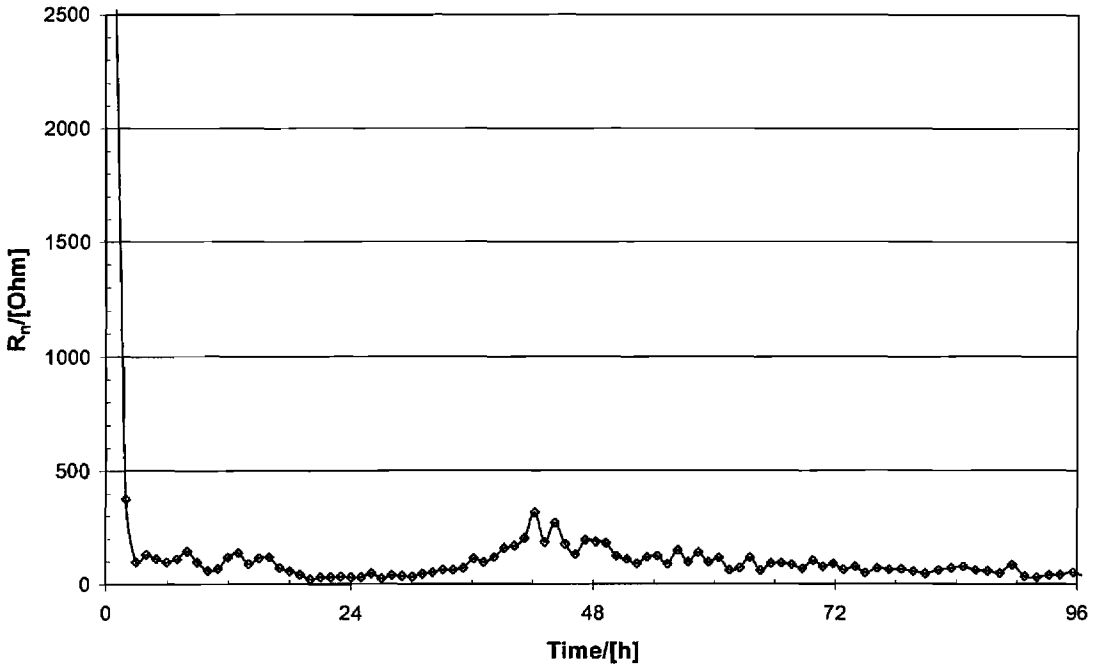


FIGURE 2(e). Noise resistance, $R_n$, in the time domain for carbon steel A516 grade 70 (UNS K02700) in Synthetic I+ solution over four days at 135°C.

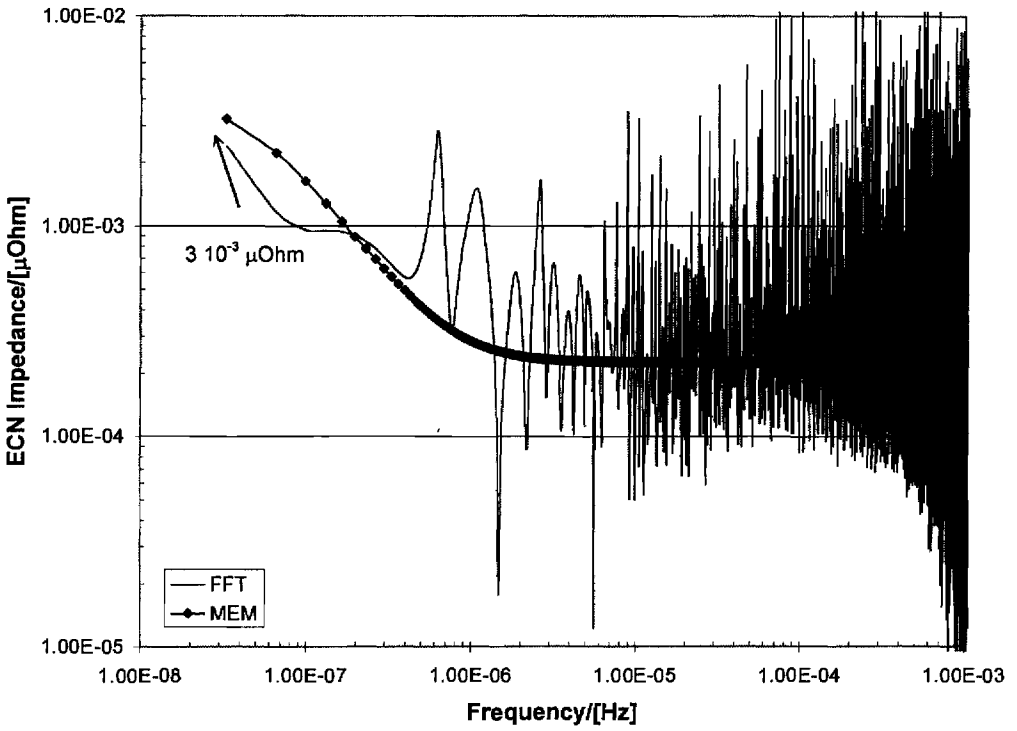


FIGURE 2(f). ECN impedance, $Z_n$, in the frequency domain for carbon steel A516 grade 70 (UNS K02700) in Synthetic I+ solution at 135°C.

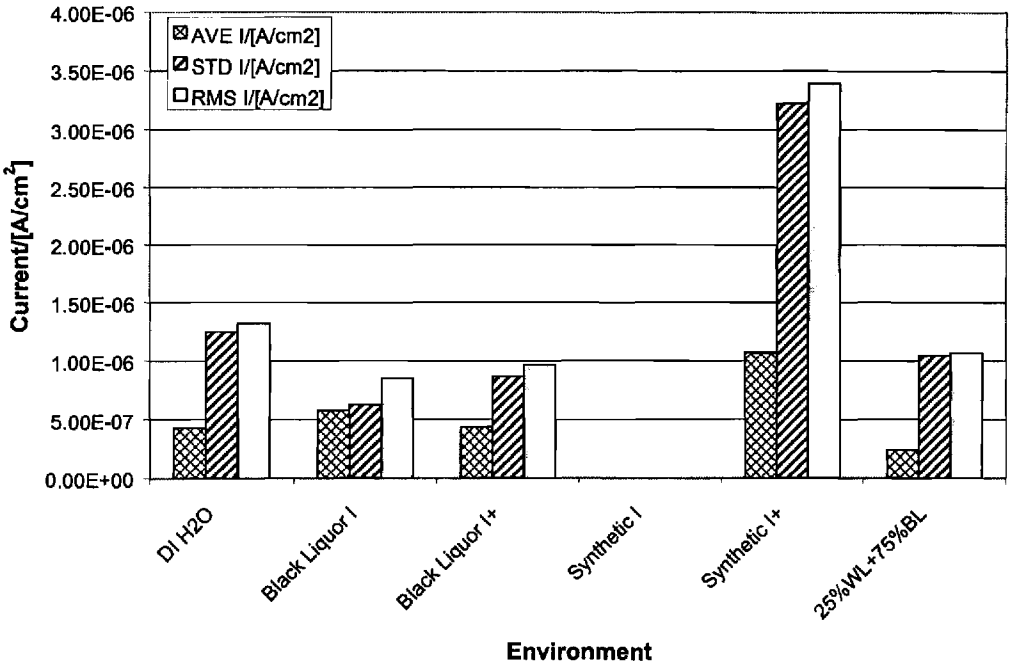


FIGURE 3(a). Absolute average, standard deviation and root mean square (RMS) current densities of carbon steel tests in stagnant conditions at 135°C for different environments.

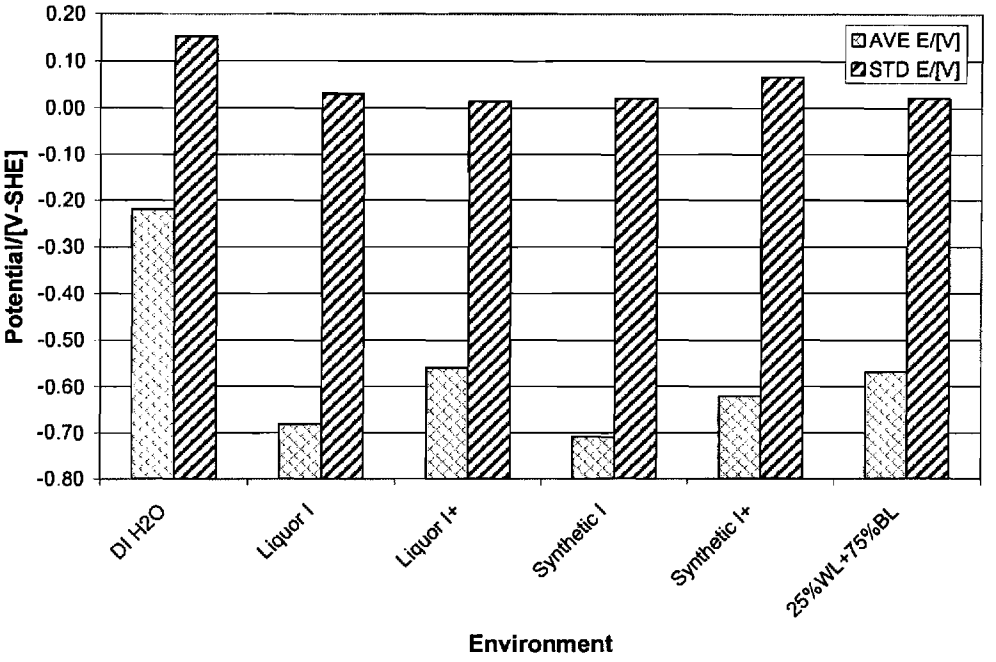


FIGURE 3(b). Average free corrosion potential and standard deviation of carbon steel tests in stagnant conditions at 135°C for different environments.

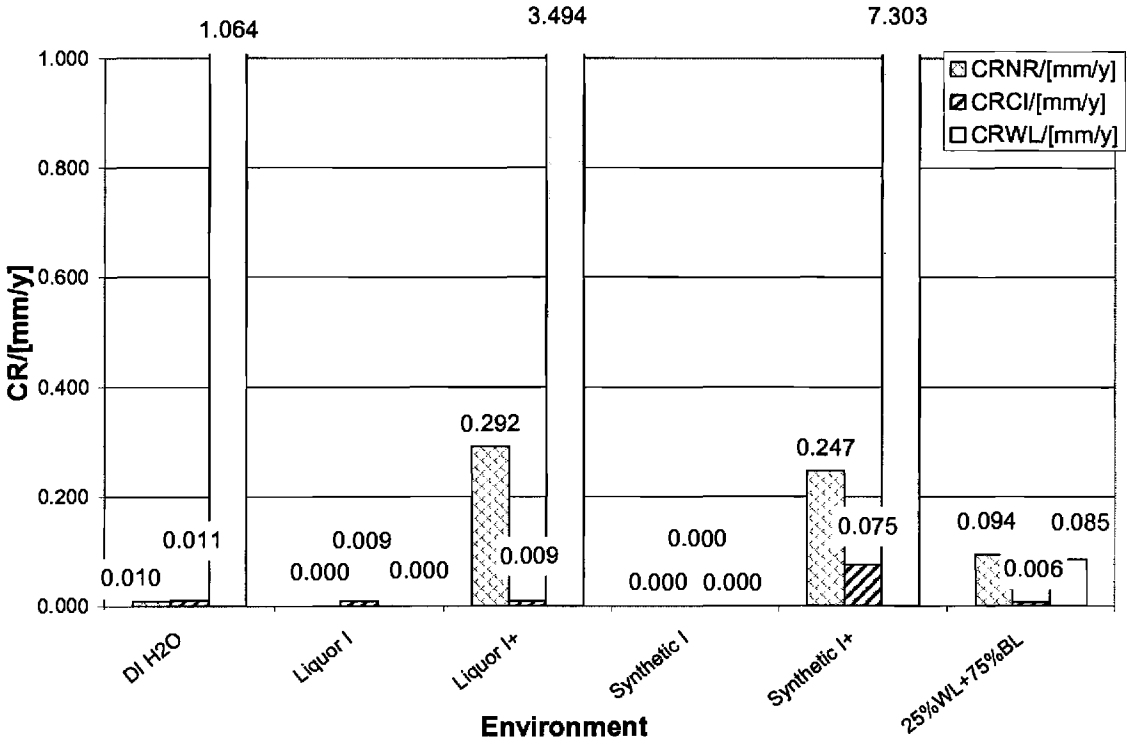


FIGURE 3(c). Corrosion rates by weight loss and current integration for carbon steel tests in stagnant conditions at 135°C for different environments.

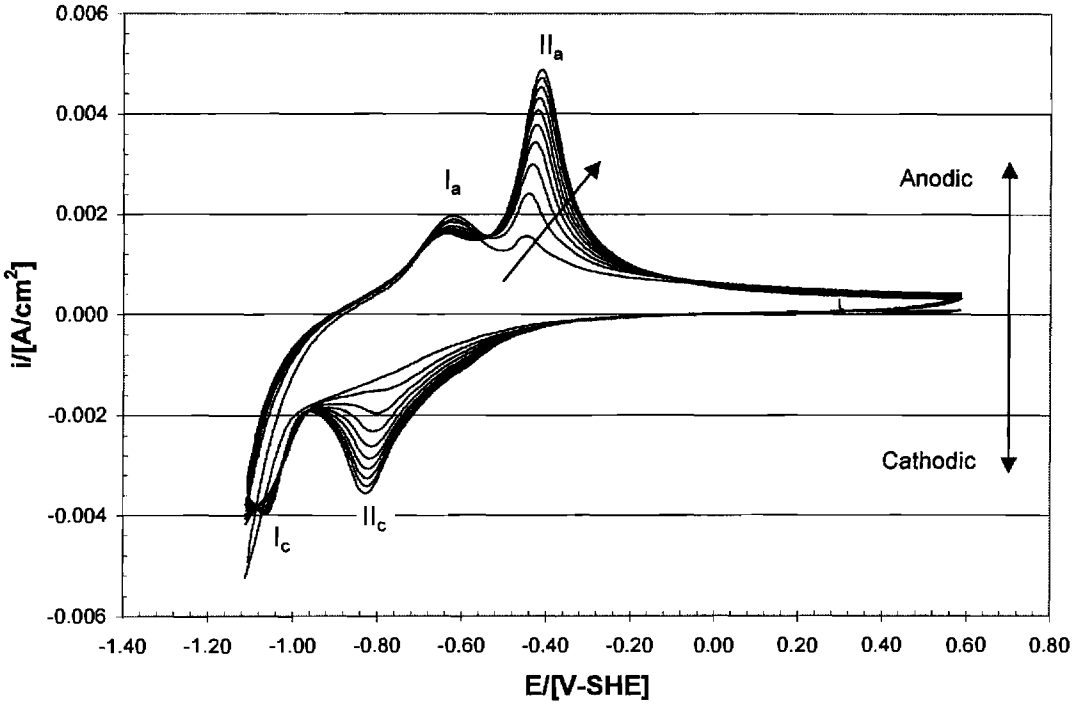


FIGURE 4(a). Cyclic voltammetry of carbon steel in 18.5 g/L NaOH at room temperature.

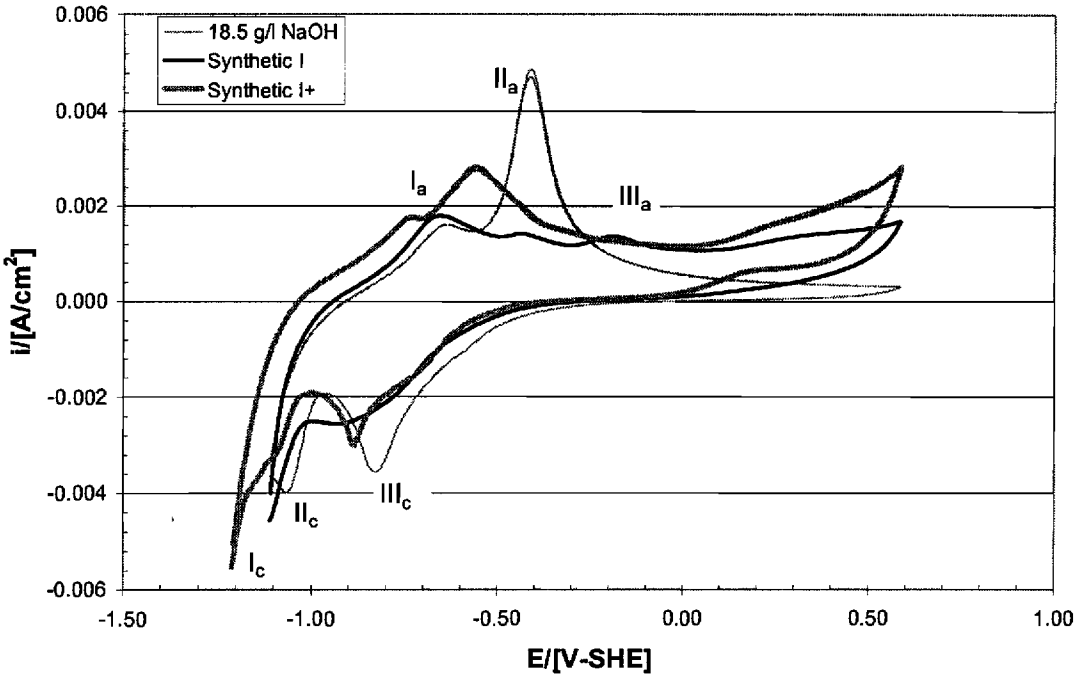


FIGURE 4(b). Cyclic voltammetry of carbon steel in 18.5 g/L NaOH, Synthetic I, and Synthetic I+ environments at room temperature.

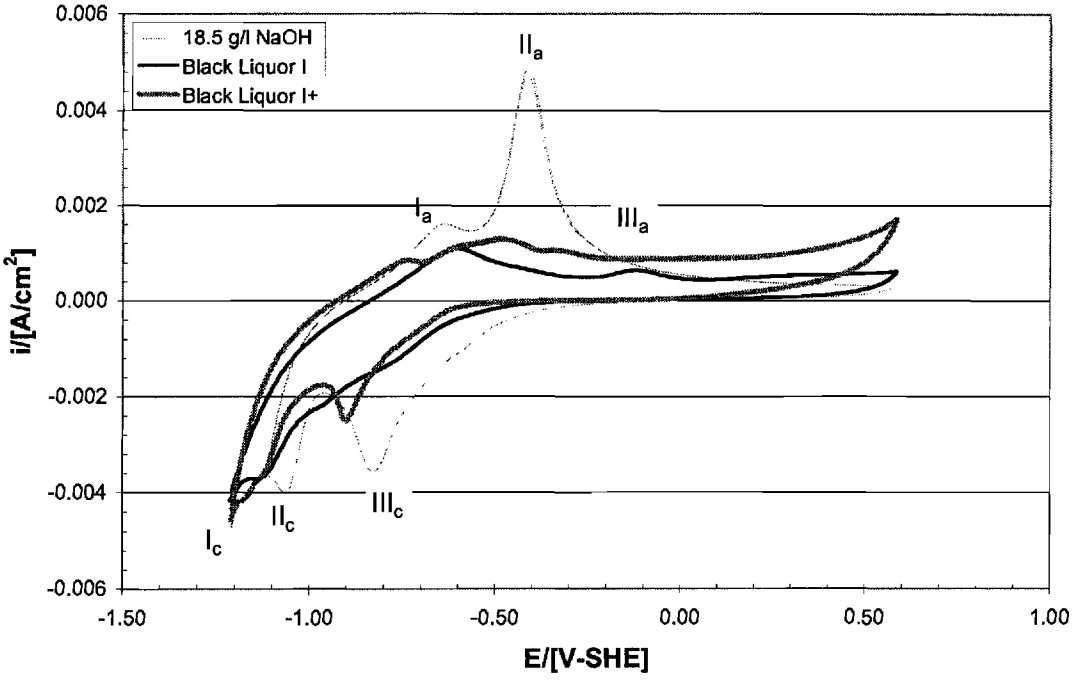


FIGURE 4(c). Cyclic Voltammetry of carbon steel in 18.5 g/L NaOH, Black Liquor I, and Black Liquor I+ environments at room temperature.